

THE EFFECT OF CO COADSORPTION ON THE HYDROGENATION PROPERTIES OF IRON

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Keywords: Iron catalysts, hydrogenation catalysts, ethylene decomposition

ABSTRACT

During the course of a series of reactions designed to examine the differences in carbon deposition characteristics exhibited by CO and C₂H₄ over iron an unexpected pattern of behavior was found. Exposure of the metal to a C₂H₄-H₂ mixture at 600°C resulted in only minor decomposition of the olefin, however, upon addition of a small amount of CO to the system, there was a dramatic increase in the amount of filamentous carbon formed, of which the major fraction could be attributed to decomposition of C₂H₄. Maximum reactivity was achieved with a C₂H₄-CO-H₂ (3:1:1) mixture and it was apparent that CO was responsible for not only promoting the formation of solid carbon, but also inducing the conversion of C₂H₄ to C₂H₆. Removal of CO from the system resulted in a rapid decline in catalytic activity, however, upon re-introduction of CO activity was restored to its initial high level, indicating that the reversible nature of the activation-deactivation processes. This behavior is rationalized in terms of a reconstruction of the iron surface in the presence of coadsorbed CO which results in the possible formation of various faces with differing reactivity characteristics, and a relaxation when CO is removed from the reactant.

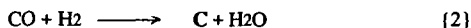
INTRODUCTION

The high activity of iron with CO has only been observed when some additive gas such as hydrogen, water vapor or other oxygenates were mixed with the reactant [1-3]. Dry and coworkers [2] reported that in all the cases where enhancement of carbon deposition was observed then hydrogen was shown to be present within the catalyst bed. They suggested that the increase in solid carbon formation was related to the ability of hydrogen to strengthen the adsorption characteristics of CO to the iron and as a consequence increase its rate of decomposition.

It is known that disproportionation of CO takes place via the Boudouard equilibrium,



which favors the right side at temperatures below 700°C. The promotional effects of hydrogen on the decomposition of CO have been interpreted in two ways. The first, the occurrence of a secondary reaction (CO hydrogenation) to produce solid carbon [1,3]:



In addition to this process, hydrogen adsorbed on the metal surface was also found to catalyze the Boudouard reaction and this effect has been explained by the ability of hydrogen to decompose inactive metal carbides into the catalytically active metallic phase [1]. There have been numerous investigations which have dealt with the interaction of CO and hydrogen on transition metal surfaces and these have been comprehensively reviewed by Vannice [4]. It is generally agreed that the uptakes of CO and hydrogen are mutually enhanced by a coadsorption procedure compared to that of either gas alone and this aspect was rationalized in terms of the formation of a surface complex between the two adsorbate molecules.

Perhaps the clearest understanding of the interaction of CO-H₂ with iron comes from recent surface science studies performed by Madix and coworkers [5,6] of the coadsorption of CO and H₂ on Fe(100) surfaces. It was suggested that adsorbed CO induced a weakening in the strength of the Fe-H bond, which triggered the formation of a potentially more reactive hydrogen species. In a subsequent investigation Burke and Madix [7] demonstrated the validity of this argument in experiments where the introduction of CO onto an iron surface pre-saturated with hydrogen brought about the formation of ethane from coadsorbed ethylene, a reaction which did not occur in the absence of CO [8].

The current investigation was undertaken in an attempt to gain a fundamental understanding of the differences in the reactivity of ethylene-hydrogen mixtures both in the absence and presence of carbon monoxide, when passed over an iron catalyst.

EXPERIMENTAL

The experiments reported here were carried out in a flow reactor system operated at 1 atm total pressure. There was provision for taking samples at various intervals during reaction for gas product analysis by gas chromatography. Powdered iron catalyst samples (50 mg) were held in a ceramic boat which was placed at the center of the reactor tube. After reduction of the sample in a 10% H₂-He mixture for 2 hours at 600°C, the system was flushed with helium and then the reactant, either pure CO, CO-H₂, C₂H₄-H₂ or CO-C₂H₄-H₂ mixtures, was introduced into the system and allowed to react with the iron catalyst at 600°C for periods of up to 5 hours. The total amount of carbon deposited during the experiment was determined by weight difference. The composition of the gas phase was monitored as a function of time from analysis performed in a Varian 3400 GC equipped with a 30 m megabore column (GS-Q). Iron powder (200 mesh) was obtained from Johnson Matthey Inc. (99.99% purity) and had a BET nitrogen surface area of 0.3 m²/g at -196°C. The gases used in this work CO (99.9%), hydrogen (99.999%), ethylene (99.99%) and helium (99.99%) were obtained from Alphagaz company and used without further purification.

RESULTS AND DISCUSSION

Iron Catalyzed Decomposition of C₂H₄-H₂ and CO-C₂H₄-H₂ Mixtures

When C₂H₄-H₂ (3:1) mixture was passed over iron at 600°C, the reactivity of the system was very low, only about 0.43% of solid carbon being produced with no detectable amounts of other products being formed. This is consistent with the notion that iron is not a very active hydrogenation catalyst in its pure form [8]. After a period of about 1 hour, CO was introduced into the feed gas in sufficient concentration to create a CO-C₂H₄-H₂ (1:3:1) mixture. The addition of CO to the reactant resulted in a dramatic increase in the percent of ethylene undergoing reaction, rising from 0.51 to 79.7%, over a 30 min period of time. It appears that the presence of CO induces changes in the surface of the iron catalyst which enhances its ability to adsorb and decompose ethylene.

In a further series of experiments, initially a CO-C₂H₄-H₂ (1:3:1) mixture was passed over an iron catalyst, and the same high levels of ethylene decomposition as those produced in the previous experiment were obtained. After 80 minutes reaction time, the CO flow was stopped and this action resulted in a dramatic decrease to around 0.5 %, a level comparable to that obtained with a C₂H₄-H₂ (3:1) mixture in the previous experiment. When the CO flow was re-introduced into the feed 45 minutes later, the percentage of ethylene undergoing reaction was restored to the original high level. This sequence of events indicates that the catalyst activation-deactivation process is reversible and the high olefin decomposition activity occurs only when CO is present in the reactant mixture.

In order to investigate the details of the influence of CO on the decomposition of ethylene, the ratio of CO in CO-C₂H₄-H₂ mixtures was varied from 0 to 1 (CO fraction = CO/(CO+C₂). The gaseous product distribution obtained with the various mixtures are presented in Table 1. Since the amount of methane produced was relatively small and that produced from CO was negligible with the feed containing a small portion of hydrogen, the error resulting from the approach should not be appreciable. Inspection of this data shows that coadsorption of CO on the iron catalyst not only promotes the formation of ethane via the hydrogenation step, but also has a tremendous impact on the fate of the carbon species produced on the metal surface from the C-C bond cleavage of the adsorbed ethylene molecules. It is known from previous studies [8] that in the absence of CO, ethylene adsorbs reversibly without dissociation on hydrogen pre-saturated iron surfaces and it is therefore not surprising to find that very little solid carbon is produced on the metal. In the presence of CO, the metal is activated towards ethylene decomposition and the carbon species formed at the surface proceed to dissolve into the bulk of the particle and eventual precipitation at the rear faces in the form of a filament. This is obviously a facile process since filamentous carbon is formed in abundance and its growth is sustained for relatively long periods of time.

When CO is removed from the reactant then the fraction of ethylene which decomposes declines to the level exhibited by the CO-free iron surface. On re-introduction of CO the amount of ethylene which is decomposed is quickly restored to a high level demonstrating the reversible nature of the promotional effect. It is possible that adsorption of CO induces reconstruction of the surface to a configuration which facilitates rupture of the C=C bond in ethylene. Elimination of CO from the system causes a relaxation of the reconstructed surface to a structure which no longer favors ethylene decomposition. It is also worth taking into consideration the possibility that the presence of CO produces electron perturbations which alter the bonding characteristics between the ethylene and metal surface atoms.

It is interesting to compare the relative amounts of methane formed in the present system with that produced from the decomposition of C₂H₄-H₂ mixtures over copper-nickel alloy particles [9] where over 20% of the ethylene decomposed to form methane. The excessive amount of methane generated in this latter system was purported to result from the formation of an "ethylidyne" intermediate. It would appear, therefore, that in the present system, where the methane yield under comparable conditions is less than 1%, the formation of an "ethylidyne" intermediate is not a favored step.

From a consideration of the product distribution it is possible to make certain speculations regarding the mode by which ethylene is adsorbed on the iron surface containing coadsorbed CO and H₂. The formation of a relatively large amount of ethane from the CO-induced hydrogenation of the olefin suggests that there is a strong tendency for the ethylene molecules to bind in an arrangement in which the C=C bond is "parallel" to the metal surface, as depicted in Figure 1a. Conversely, the low amount of methane produced during this reaction indicates that there is a reluctance for ethylene to adsorb in the "end-on" configuration, where one of the carbon atoms in the molecule is attached to three metal atoms in the form of an "ethylidyne" conformation, as illustrated in Figure 1b.

CONCLUSIONS

In the present investigation ethylene was used as a model hydrogen acceptor molecule. It was found that iron exhibited very little activity for the hydrogenation of the olefin, however, when as little as 7% CO was added to the hydrocarbon-hydrogen mixture, the hydrogenation activity of the metal was substantially enhanced. Such an increase in hydrogenation activity was observed over a wide range of temperature, however, at 600°C one has to contend with the concomitant formation of a large amount of solid carbon. The presence of coadsorbed CO induces a weakening in the strength of the metal-hydrogen bond, which gives rise to the formation of a very reactive hydrogen species. These model studies demonstrate that the introduction of a gas additive, such as CO, into the reactant stream can effectively convert a metal which in its pure state is relatively inert into an

extremely active hydrogenation catalyst, and we believe that this concept could be extended to hydrogenation of coal and its derivatives.

ACKNOWLEDGMENTS

Support for this work was provided by the National Science Foundation, under Grant CBT-8800931.

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TABLE 1. EFFECT OF GAS COMPOSITION ON THE GASEOUS PRODUCT DISTRIBUTION FROM THE INTERACTION OF C₂H₄-CO-H₂ MIXTURES OVER IRON AFTER 60 MINUTES AT 600°C

C ₂ H ₄ :CO:H ₂	% C ₂ H ₄ Decomposition	% CH ₄ formed	C ₂ H ₆ formed
80:0:20	0.51	-	-
73:7:20	29.53	0.73	8.5
68:12:20	60.28	0.58	9.4
60:20:20	79.47	1.07	10.3
38:42:20	76.10	2.7	5.5
17:63:20	54.30	2.6	5.8
0:80:20	21.95	0.05	--

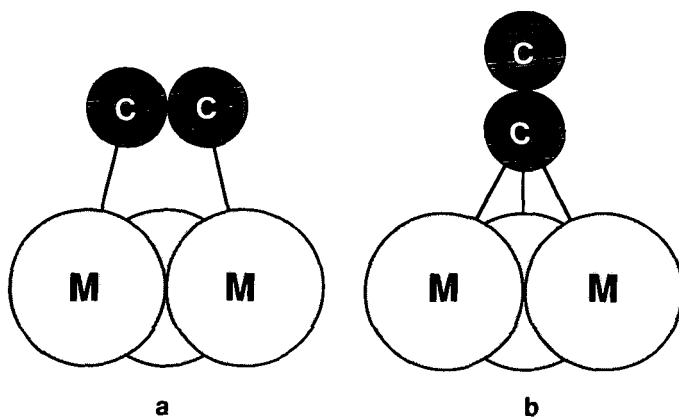


FIGURE 1. STRUCTURAL ARRANGEMENT FOR (a) ETHYLENE BONDED PARALLEL TO METAL SURFACE AND (b) ETHYLENE BONDED TO METAL IN THE STABLE "ETHYLIDYNE" CONFORMATION